

**IN THE SPECIFICATION**

Please amend the specification as indicated below, deleting text marked with strike through and adding the underline text. The paragraph numbers refer to the specification as published in U.S. Published Patent Application No. 20050164092.

After the title of the invention and before paragraph [0001] please insert the following section header:

**BACKGROUND OF THE INVENTION**

**Field Of The Invention**

After the paragraph [0002] and before paragraph [0003] please insert the following section header:

**Description of Related Art**

After the paragraph [0006] and before paragraph [0007] please insert the following which ends with the insertion of the section header "DETAILED DESCRIPTION":

**BRIEF SUMMARY OF THE INVENTION**

The present inventive subject matter is related to organic solutions containing metal(IV) salts and oxoacids of phosphorus from which, after evaporation of the solvent, insoluble compounds of general composition  $M(IV)(O_3P-G)_2 \cdot n(O_3P--R^1--X)_n$  can be obtained, where M(IV) is a

tetravalent metal, -G is a generic inorganic or organic group, --R<sup>1</sup>-- is an organic group, --X is an acid group and n is a coefficient ranging from 0 to 1.5.

The tetravalent metal salt of these organic solutions can be an anion and is preferably chosen among carboxylates, chlorides and alkoxides. Further, the tetravalent metal salt is preferably chosen between Zr, Ti, Sn and Ce or their mixture. Further still, the tetravalent salt is preferably the zirconyl propionate or chloride.

The group -G of the organic solutions is preferably chosen among the acid groups --OH; --R<sup>2</sup>--SO<sub>3</sub>H and --R<sup>2</sup>--PO<sub>3</sub>H<sub>2</sub>, where --R<sup>2</sup>-- is an organic group with preferably linear chain such as --(CH<sub>2</sub>)<sub>m</sub>-- and --(CF<sub>2</sub>)<sub>m</sub>--.

The group --R<sup>1</sup>-- of the organic solutions is an arylene group chosen preferably among --C<sub>6</sub>H<sub>4</sub>--; --C<sub>6</sub>H<sub>4</sub>--CH<sub>2</sub>-- and --C<sub>6</sub>H<sub>4</sub>--CF<sub>2</sub>--.

The acid group --X of the organic solutions is chosen between --SO<sub>3</sub>H, --PO<sub>3</sub>H<sub>2</sub> and --COOH.

The solvent may be an inorganic solvent and is chosen among the protonable solvents, especially N,N-dimethylformamide, N-methyl-2-pyrrolidone, dioxane, dimethylsulfoxide, acetamide, acetonitrile, various alkanols and/or their mixtures, commonly used for dissolving the proton conducting ionomers of the state of art.

A further embodiment of the current inventive subject matter is the use of these

organic solutions for the insertion of nanoparticles of tetravalent metal salts, preferably phosphate-phosphonates, within the pores of polymeric or inorganic porous membranes.

Likewise, methods for the filling of porous membranes with tetravalent metal salts are also contemplated, especially phosphate-phosphonates, based on the following steps: a) preparation of the organic solution described herein, at the same time, may also contain a polymer and/or an ionomer of the state of the art; b) impregnation of the porous membrane with such a solution; c) elimination of the solvent; d) repetition of the steps b and c until the wished percentage of pore filling is obtained.

Even a further embodiment of the current inventive subject matter are proton conducting composite membranes made of polymeric or inorganic porous membranes with pores filled with tetravalent metal salts, especially phosphate-phosphonates, or mixtures of said compounds with a proton conducting ionomer and especially prepared by using the organic solutions described herein.

Likewise, such proton conducting composite membranes wherein the polymeric porous membrane is preferably chosen between those made of chemically and/or thermally stable polymers, especially polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), polyesters, polyethersulfones and fluoroelastomeres are also

contemplated. The proton conducting composite membranes described herein wherein the pore dimensions of the porous membranes are preferably in the range 0.02-20  $\mu\text{m}$ , especially 0.1-10  $\mu\text{m}$ , preferably 0.4-2  $\mu\text{m}$  and the porosity >10%, especially >50%, preferably 65-90% are also provided for.

Even further still, proton conducting composite membranes as described herein wherein the tetravalent metal salts, preferably phosphate-phosphonates, for the filling of pores are chosen between  $\text{Zr}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_2$  and compounds of the series  $\text{Zr}(\text{O}_3\text{P}-\text{OH})_{2-n}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_n$ , and  $\text{Zr}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_{2-n}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_n$ , with  $n$  in the range 0.1-1.5 are contemplated. Also, composite membranes made up of a porous ceramic membrane partially filled with a tetravalent metal salt, preferably phosphate-phosphonate, as described herein and exhibiting catalytic activity are also contemplated. Specifically, composite membranes made up of porous ceramic membranes partially filled with tetravalent salts, preferably phosphate-phosphonate, are chosen between  $\text{Zr}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_2$  and compounds of the series  $\text{Zr}(\text{O}_3\text{P}-\text{OH})_{2-n}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_n$ , and  $\text{Zr}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_{2-n}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_n$ , with  $n$  in the range 0.1-1.5 with catalytic activity are also contemplated.

The use of the organic solutions as described herein for the preparation of nano-polymers constituted by nano-particles of

tetravalent metal salts as described herein, preferably phosphate-phosphonates, dispersed in the matrix of organic or inorganic polymers soluble in the same solvents is contemplated. Likewise, the use of the organic solutions as described herein for the preparation of the nano-polymers described herein wherein the organic polymeric matrix is that of a proton conducting ionomer is also provided for.

Also provided for are methods for the preparation of nano-polymers and nano-ionomers as described herein based on: a) preparation of an organic solution as described herein and at the same time containing a polymer and/or an ionomer of the state of the art; b) elimination of the solvent. These methods described herein also provide for the preparation of nano-polymers and nano-ionomers as described herein wherein the elimination of the solvent is preferably performed by evaporation or with a non-solvent of the polymer or ionomer.

Also contemplated are nano-polymers constituted by nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, dispersed in the matrix of organic or inorganic polymers. These nano-polymers as described herein wherein the polymeric matrix is that of a synthetic ionomer of the state of the art preferably chosen among perfluorosulphonic polymers, sulfonated polyetherketones (sPEK), sulfonated polyethersulfones and sulfonated

polyvinylidenefluoride (SPVDF) are also provided for, as are the nano-polymers as described herein wherein the nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, dispersed in the polymeric matrix are chosen among those exhibiting proton conductivity  $>10^{-2}$  S  $\text{cm}^{-1}$  at 70°C. and 95% relative humidity. Further still, these nano-polymers as described herein wherein the nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, are chosen between  $\text{Zr}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_2$  and compounds of the series  $\text{Zr}(\text{O}_3\text{P}-\text{OH})_{2-n}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_n$ , and  $\text{Zr}(\text{O}_3\text{P}-\text{C}_6\text{H}_4-\text{SO}_3\text{H})_{2-n}(\text{O}_3\text{P}-\text{CH}_2-\text{PO}_3\text{H}_2)_n$ , with  $n$  in the range 0.1-1.5 with catalytic activity are also contemplate

The use of the organic solutions as described herein for an easy insertion of a large variety of lamellar nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, in the membrane/electrode interfaces of PEM FCs is also provided for. Also, the use of the organic solutions as described herein, with the addition of ionomers and/or other proton conducting compounds soluble in the same solvents, for an easy insertion of a large variety of lamellar nano-particles of tetravalent metal salts, preferably phosphate-phosphonates, in mixture with other proton conducting compounds in the membrane/electrode interfaces of PEM FCs is also contemplated.

Further still, the use of proton conducting

membranes constituted by inorganic or polymeric porous membranes with pores filled with tetravalent metal salts, preferably phosphate-phosphonates, as described herein and of membranes constituted by nano-polymers as described herein, in electrochemical devices is also contemplated. The use of proton conducting membranes as described herein in electrochemical devices specifically planned for generating electrical energy from the oxidation of a fuel is also provided for, as is the use of proton conducting membranes of as described herein in fuel cells specifically planned for electrical vehicles and/or for portable electrical devices. Also provided for are the uses of composite membranes as described herein for improving the global performance of ionomeric membranes of the state of the art in hydrogen, indirect methanol and direct methanol fuel cells and the use of the membranes described herein in catalytic membrane reactors.

#### **Brief Description Of The Figures**

Figure 1 a) The typical layered  $\alpha$ -structure of organic derivatives of the corresponding layered metal(IV) phosphates

Figure 1 b) Shows a schematic view of a single lamella of the compound  $\text{Zr}(\text{O}_3\text{P}-\text{G})(\text{O}_3\text{P}-\text{G}-\text{X})$  where  $\text{G}=\text{---OH}$ ;  $\text{---R}^1\text{---C}_6\text{H}_4\text{---}$ ;  $\text{---X}=\text{---SO}_3\text{H}$ .

DETAILED DESCRIPTION

Please amend paragraph [0010] as follows:

[0010] It is well known that metal(IV) phosphate-phosphonates are members of a very large family of lamellar compounds. They can be seen as organic derivatives of the corresponding layered metal(IV) phosphates among which the most investigated compound is the zirconium phosphate,  $\text{Zr}(\text{O}_3\text{P--OH})_2$ , exhibiting the typical layered  $\alpha$ -structure, schematically illustrated in FIG. 1a. The compositions of possible metal(IV) phosphate-phosphonates can be very different from each other since the phosphonate groups can be chosen among a large variety of species and even their mixtures in different ratios can be used. Thus, for sake of brevity, when a more precise definition of the composition is not necessary, the zirconium phosphate-phosphonates will be here simply indicated by the general formula  $\text{M(IV)}(\text{O}_3\text{P--G})_{2-x}(\text{O}_3\text{P--R}^1\text{X})_n$  where  $\text{M(IV)} = \text{Zr, Ti, Sn or Ce}$ ; G is an inorganic (e.g., --OH) or organic (e.g., --CH<sub>2</sub>OH) or an inorganic-organic group (e.g., --CH<sub>2</sub>--SO<sub>3</sub>H; --CF<sub>2</sub>--PO<sub>3</sub>H<sub>2</sub>); R<sup>1</sup> is an ~~arylen~~ arylene group (e.g., phenylen); X is an acid group chosen between --SO<sub>3</sub>H, --PO<sub>3</sub>H<sub>2</sub> and --COOH; n is a coefficient which can vary between 0 and about 1.5. In this formulation, the O<sub>3</sub>P-- (i.e. written with the three oxygens to the left of phosphorus)



indicates that each phosphorus is bonded to three different zirconium atoms through three oxygens, as in the lamellar structure of  $\alpha$ -zirconium phosphate. As an examples a schematic view of a single lamella of the compound  $\text{Zr}(\text{O}_3\text{P}--\text{OH})(\text{O}_3\text{P}--\text{C}_6\text{H}_4--\text{SO}_3\text{H})$  (i.e., where  $G=--\text{OH}$ ;  $--\text{R}^1---=\text{C}_6\text{H}_4--$ ;  $-X=--\text{SO}_3\text{H}$ ) is shown in part (b) of FIG. 1.